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Progress Report

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AN EVALUATION OF ETTRINGITE AND RELATED COMPOUNDS FOR USE IN SOLAR ENERGY STORAGE

Leslie J. Struble and Paul W. Brown
Center for Building Technology
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July 1, 1984

SUMMARY

This report describes an investigation of ettringite and related phases for potential application in solar energy storage. The specific objective is to evaluate the potential of ettringite dehydration and rehydration as a phase change process for energy storage.

Synthesis procedures have been developed, and a number of ettringite-type phases have been prepared. The heat capacity of each phase was approximately 0.3 calories per gram per degree Celsius. Studies of the dehydration of these phases at atmospheric pressure indicate that the material has good potential as a phase change material for solar energy storage. Dehydration occurred at temperatures in the range between approximately 30°C and 55°C, with changes in enthalpy ranging between 100 and 240 calories per gram of sample. In addition, ettringite was found to have a reversible hydrothermal reaction at approximately 50°C, with an enthalpy change of approximately 4 calories per gram sample.

Future work during the remainder of this program will involve completing the work described in the present progress report.

I. INTRODUCTION

Effective utilization of solar energy in the passive mode requires the utilization of materials in which either sensible or latent heat may be stored. One class of materials that holds promise for this application is hydrated salts, an example of which is ettringite, also called Candlot's salt, a hydrated calcium alumino-sulfate that forms during the hydration of portland cement. Therefore, a laboratory study is being carried out in order to evaluate ettringite and related phases for possible application in passive solar energy systems. Preliminary studies indicated that ettringite dehydration has potential for thermal energy storage (1). Further work, described in the present report, has focussed on the synthesis of ettringite and several related phases, and the determination of their thermal properties.

A. ENERGY STORAGE MATERIAL

Solar energy storage materials have two basic functions: to store solar energy, and to release it at the appropriate time. To carry out these functions, storage systems may rely on the specific heat of a material, and may also rely on a phase change which occurs in the material. In general, the amount of energy that a material is capable of storing and releasing is significantly greater if a phase change is involved. On the other hand, the phase change may bring about other changes, such as physical degradation, that limit the usefulness of the material in this application.

Specific heat, or more precisely thermal capacity, is a fundamental and measurable property (though it varies somewhat with temperature). Values of specific heat, i.e. the thermal capacity of the material relative to that of water, range considerably. The thermal capacity of water is 1 calorie per gram per degree Celsius, while thermal capacities of solids are somewhat lower, typically a few tenths calorie per gram per degree.

There is also a change in heat, or enthalpy, associated with any phase change -- including melting, changes in crystal structure, dehydration, and dissolution. The enthalpy change may be positive, such that heat is consumed (endothermic) or negative, such that heat is released (exothermic). If the phase change is reversible, then the enthalpy change is also reversible. Therefore a reversible phase change may be used for solar energy collection. The phase change utilized most extensively is melting, and an example is the melting of Glauber's salt, $Na_2SO_4 \cdot 10H_2O$. The change in enthalpy due to a phase change is a measurable property of the material (e.g., 80 calories per gram for the melting of ice, and 60 calories per gram for the melting of Glauber's salt).

However, other parameters associated with phase changes are not fundamental properties. The kinetics of the change, and therefore the precise temperature at which the change occurs at a reasonable rate, may vary considerably with the nature of the sample -- the amount of material, its particle size, etc. The temperature of a phase change is particularly important in passive solar devices, where the operating temperature is limited. Therefore, the kinetics

and the temperature of a phase change, as well as the enthalpy, must be considered in the evaluation of any material for use in solar energy collectors.

Finally, there are several other considerations when evaluating a material for this application. For instance, the physical and chemical durabilities are critical. The material must be reasonably low in cost and readily available. It must be easily and safely handled. While these factors were not the focus of the present study, they were considered throughout the study.

B. ETTRINGITE

Ettringite is a hydrated calcium alumino-sulfate, $[Ca_6Al_2(OH)_{12}](SO_4)_3 \cdot 26H_2O$, which typically forms from reaction of $Ca_3Al_2O_6$ with gypsum ($CaSO_4 \cdot 2H_2O$) and water. The dehydration, or partial dehydration, of ettringite and related phases is the particular focus of these studies. The material is known to dehydrate partially at relatively low temperatures, and the dehydration is expected to be reversible. Therefore, ettringite dehydration offers potential as a phase change process for solar energy.

The crystal structure of ettringite was described by Moore and Taylor (2) in 1970, and the structures of ettringite and related phases were subsequently reviewed by Taylor (3). The phase is hexagonal in structure, and typically occurs as a prism or needle, elongated parallel to the c-axis. The basic structural unit is a column of hydrated calcium aluminate hydroxide (Fig. 1a). The columns, positively charged, are arranged parallel to the c-axis of the crystal, with four such columns per unit cell (Fig. 1b). The negative (SO_4) ions and the remaining water molecules are found within the channels formed by these columns (Fig. 1c). The structural formula may thus be written $[Ca_3Al(OH)_6 \cdot 12H_2O]_4(SO_4)_6 \cdot 4H_2O$.

The ettringite structure is very open, and considerable chemical substitution may occur. Based on the crystal structure, however, certain restraints on the substitution are expected. For instance, the substitution for the sulfate ions would be limited by the need to balance the positive charge of the columns, and by the available space within the channels. Substitution within the columns, on the other hand, would be limited primarily by the 6-fold coordination of the aluminum and calcium within the columns.

Several types of chemical substitution have been reported within the channel sites. For instance, CO_3 may replace SO_4, either partially (3) or completely (4). In an early reference, Flint and Wells (5) reported substitution of SiO_3 for SO_4. Finally, substitution of Cl, a monovalent ion, for SO_4 has been reported (6). However, it is not clear from structural considerations whether monovalent ions may substitute for SO_4. The crystal structure analysis suggests that there are not sufficient sites within the channel for the number of monovalent ions that are required for charge balance.

Several substitutions have been described within the columns. Either Sr or Pb may substitute for Ca (3). The following elements have been reported to substitute for Al: Ge (3); Fe, Mn (3,7); Ti (7); Cr (7,9,10); and Si (3,10). The mineral thaumasite is a doubly substituted ettringite, in which CO_3 is

partially substituting within the channel, and Si is substituting for Al, requiring 6-fold coordination of Si.

The ettringite structure thus contains three distinct types of water molecules: 1) water within the channel, 4 molecules per structural unit, 2) water bound to the columns, 48 molecules per structural unit, and 3) water as hydroxide ions on the columns, 12 molecules per structural unit. It is reasonable to expect the conditions for dehydration and the structural changes associated with dehydration to be different for each of the three types of water.

Dehydration may be carried out at room temperature and atmospheric pressure by reducing the partial pressure of water in the system. As reviewed by Lea (11), this dehydration is reported to proceed with no change in X-ray diffraction pattern until there are 36 molecules of water per structural unit. This loss presumably corresponds to the loss of the 4 molecules of water from within the channel and the loss of 24 of the 48 molecules that are bound as water on the columns. Further dehydration causes a change in the X-ray diffraction pattern, i.e. a shift in the basal peak from 0.97 nm to 0.73 nm, until 16 molecules of water remain, corresponding to loss of most of the remaining water from the channels.

In some cases, dehydration at elevated temperature produces similar behavior. Taylor (3) described changes on heating at 110°C, during which shrinkage was observed along the a-axis, until a = 0.84 nm. He suggested that dehydration resulted in the individual columns coming closer together to produce the shorter a-axis. However, a few studies have reported quite different results. Mehta (12) found that heating in a dry environment to 94°C caused no changes in the XRD pattern, including no shrinkage of the a-axis. Likewise, Sudoh et al. (13) reported that heating at 100°C caused ettringite to become amorphous but produced no shrinkage of the structure. Thus there is some conflict in the literature regarding the effects of thermal dehydration on the crystal structure.

The behavior is quite different when ettringite is heated under hydrothermal conditions. In that case, the ettringite decomposes to hydrated calcium monosulfoaluminate, (12, 14). Hydrothermal dehydration was studied by Satava and Veprek (14) using differential thermal analysis under hydrothermal conditions. They found that in liquid water, ettringite converted to calcium monosulfoaluminate and calcium sulfate hemihydrate in an endothermic reaction at 150°C.

Far less information is available regarding thermal properties other than temperature. Especially important in energy storage is whether the reaction is reversible. Although no information was found, it is expected that if the dehydration causes no change in crystal structure, it will be readily reversible. No information was found regarding the enthalpy changes associated with any of the dehydration reactions. One study of the heat capacity of ettringite reported c_p values of 0.41 calories per gram (15)

The limited information supports the hypothesis that dehydration of ettringite provides a potential phase change for solar energy storage. The dehydration of ettringite occurs at a sufficiently low temperature, the reaction may be reversible, and the large number of possible chemical substitutions provides

opportunity for optimizing thermal properties. Therefore, ettringite and related phases were synthesized and their thermal properties determined experimentally.

II. EXPERIMENTAL PROCEDURE

During the preliminary studies (1), phases were synthesized by slow reaction of $Ca_3Al_2O_6$ or a similar material with water and some form of calcium sulfate. For the more detailed studies, however, procedures were developed in which the reactants were first dissolved, and then mixed. In this way, the reactions proceed faster, typically complete within a day, rather than several days or weeks. Furthermore, reactants in solution produce a more homogeneous product and allow better control of the reacting constituents.

In general, the syntheses started with solutions of the desired reactants in stoichiometric proportions, using as high a concentration as possible. One solution contained one cation (aluminum, iron (III), etc.), and the desired ion (sulfate, carbonate, chloride, etc.). The calcium solution was prepared separately, by dissolving CaO (prepared by igniting reagent $Ca(OH)_2$) in a 10% sugar solution. The sugar allowed significantly higher concentrations of calcium (0.3 M with sugar, 0.02 M without sugar). When these two solutions were mixed, precipitation usually began within an hour. Solutions were rotated at room temperature for a few hours or a day, filtered, and the precipitates washed with water and ethanol, then dried under reduced pressure.

Because CO_3 is a possible substituting ion in ettringite, specific measures were taken during synthesis to avoid unwanted carbonation. All solutions were prepared in freshly boiled water. Reactions were carried out in closed containers, in which air was first displaced by N_2 gas. The relatively short reaction times made it easier to avoid carbonation.

Ettringite is known to be unstable -- to undergo partial dehydration (or rehydration) at room temperature, depending on the water vapor pressure. Therefore, care was taken that all material be in equilibrium with some constant environment prior to the characterization and the thermal studies. After synthesis and drying in a mild vacuum, each sample was ground to -325 mesh. Specimens were then stored over a saturated $ZnCl_2$ solution, at a nominal water vapor pressure of 28% RH.

Reaction products were characterized by X-ray diffraction. In a few cases, qualitative chemical analysis was also necessary.

B. THERMAL STUDIES

Heat capacity (c_p) was measured by Differential Scanning Calorimeter (DSC), equipped with a microprocessor for control and computer software for data collection and analysis. Scans for c_p were collected over a temperature range below the dehydration reaction. The instrument was calibrated for C_p using a standard sample of sapphire.

Thermal studies of the dehydration reaction at atmospheric pressure were carried out in order to determine the temperature, the amount of water lost, and the enthalpy change. These studies utilized both Thermal Gravimetric Analysis (TGA), also with microprocessor and computer, and the DSC. Both these methods are known to be highly sensitive to experimental conditions. In particular, the transition temperature is highly sensitive to the rate of heating. In order to determine the thermal properties precisely and accurately, the measurements were carried out at the very slow heating rate of 0.6° per minute. Both TGA and DSC samples were run in open pans, in order to improve precision. Finally, very small amounts of sample were used, typically 1 mg.

The DSC and TGA studies provided thermal data -- dehydration temperature, weight loss, and enthalpy changes -- but no information about the kinetics of the dehydration. Therefore one relatively large sample (several grams) was dehydrated at 60°C in order to determine its rate of dehydration. In addition, partially dehydrated specimens from this experiment were analyzed by X-ray diffraction, in order to determine whether partial thermal dehydration causes any changes in the crystal structure.

Studies of the rehydration of partially dehydrated specimens were carried out in a hydration calorimeter, which was designed and built at NBS (16). This calorimeter allows much more sensitive and accurate measurement of enthalpy changes than the calorimeter that was used for the preliminary studies (1). Samples were first partially dehydrated in an oven, then mixed with water in the calorimeter.

Some enthalpy changes were measured under hydrothermal conditions, using high-pressure DSC cells, with the sample covered by water. This reaction could be reversed while still in the DSC, so a single specimen could be dehydrated and rehydrated repeatedly. This method avoids the experimental problems described above, and provides a very precise estimation of the number of dehydration/rehydration cycles before degradation for the hydrothermal reaction.

III. RESULTS AND DISCUSSION

A. SYNTHESIS AND CHARACTERIZATION OF PHASES

Several procedures were explored for synthesis of ettringite and related phases, most following the general method of mixing reactants in solution form. The following substitutions were attempted: CO_3 for SO_4, Cl for SO_4, NO_3 for SO_4, Fe (III) for Al, Cr (III) for Al, and Si for Al. General aspects of each procedure are provided in this section, and details are given in Appendix A.

The primary procedure for preparation of ettringite was to mix a solution of $Al_2(SO_4)_3$ (1 M) with a solution of CaO (0.3 M). Precipitation began as soon as the solutions were mixed, approximately 20% of the theoretical yield was obtained after reacting overnight, and approximately 30% of the theoretical yield after reacting for several days. The only reaction product observed by X-ray diffraction was ettringite.

A similar procedure was used to prepare several substituted phases. For Fe-substituted ettringite, a slurry of $Fe_2(SO_4)_3$ was used, since this phase is much less soluble than the aluminum salt, and this slurry mixed with a solution of CaO (0.3 M). Likewise, Cr-substituted ettringite was prepared from a solution of $CrK(SO_4)_2$ (4 M) and a solution of CaO (0.2 M). In each case, the only reaction product observed by X-ray diffraction was an ettringite-like phase.

A similar procedure was tried for substituting monovalent ions for SO_4. To prepare the Cl-substituted phase, a solution of $AlCl_3$ (0.9 M) was mixed with a solution of CaO (0.3 M). In this case, the reaction product was not an ettringite phase, but rather a Cl-substituted monosulfate, $[Ca_2Al(OH)_6]_2(SO_4)\cdot 6H_2O$. Likewise, a solution of $Al(NO_3)_3$ (0.8 M) mixed with a solution of CaO (0.3 M) produced an amorphous reaction product. Partial substitution with each monovalent ion was also unsuccessful. Ettringite-type phases were produced, but qualitative chemical analysis of each phase showed it to be unsubstituted ettringite.

Another successful procedure for preparation of ettringite was to mix a solution of $Na_2Al_2O_4$ (0.3 M) and Na_2SO_4 (0.3 M), with a solution of CaO (0.3 M). This provided a general procedure that was easily modified for the CO_3-substituted phase, by replacing Na_2SO_4 with $NaHCO_3$. Again, the only reaction product observed by X-ray diffraction was an ettringite-like phase.

Preparation of thaumasite was attempted from a solution of Na_2SiO_3 (0.5 M) with Na_2SO_4 (0.5 M) and $NaHCO_3$ (0.5 M), and a solution of CaO (0.3 M). The resulting mixture was held at 5°C, as was suggested by van Aardt and Visser (17) in order to achieve the required 6-fold coordination of Si. However, the precipitate formed during this reaction was not thaumasite, but was amorphous to X-rays.

In summary, synthesis procedures were developed using solutions, which fulfilled the initial objectives that the reaction be rapid, the product homogeneous, and carbonation be prevented. These procedures allowed synthesis of ettringite and ettringite-like phases with various chemical substitutions, including CO_3 for SO_4, Fe for Al, and Cr for Al. The procedures did not allow substitution of Si for Al or Cl or NO_3 for SO_4.

B. HEAT CAPACITY

Measured heat capacities (Table I) were approximately 0.3 calories per gram per degree Celcius. There was no significant difference in heat capacity for any of the phases tested.

C. DEHYDRATION

TGA and DSC results are given in Table II. In general, the dehydration occurred over a temperature range from approximately 30°C to approximately 55°C. This upper temperature was lowest (49°C) for the CO_3-substituted ettringite phase and highest (58°C) for the Fe-substituted phase.

Water loss averaged approximately 20 moles of water per mole of sample, or 40 moles relative to the structural formula. This corresponds to all the water in the channels and approximately 75% of the water bound to the columns.

The change in enthalpy for these dehydration reactions varied from 100 calories per gram sample for the CO_3-substituted phase to 230 calories per gram sample for the Fe-substituted phase. It should be noted that the changes in enthalpy are extremely dependent on the experimental conditions -- sample size, type of specimen cell, etc. Enthalpy change of one material has been found to vary by as much as 100% with different experimental conditions. Therefore, it is important to assess the precision of the enthalpy change before concluding that substituted phases have significantly different enthalpy changes. At any rate, these enthalpy changes are significantly higher than the value (60 calories per gram) observed for the melting of Na_2SO_4, a phase change material used in solar energy collection.

As expected, the dehydration at 56°C of a large sample occurred more slowly than the dehydration of very small samples in the TGA and DSC experiments. The TGA sample of 1 mg showed 27% loss by 51°C (at 0.6°/min, this temperature was reached in 40 minutes). Several grams of the same material heated in an oven at 56°C had only 14% loss in 72 hours (Fig. 2). However, heating at a higher temperature increased the rate of dehydration dramatically. A large sample of ettringite heated at 110°C showed a weight loss of 24% after 1 hour and 31% after 2 hours.

Heated samples were analyzed by X-ray diffraction for any changes in the crystal structure or unit cell parameters. Progressive dehydration caused the sample to become increasingly amorphous to X-rays but with no observed changes in unit cell parameters. The samples heated at 56°C were mixtures of ettringite and amorphous material, and the samples heated at 110°C were entirely amorphous.

Ettringite and a sample of partially dehydrated ettringite were examined by scanning electron microscopy (Fig. 3). The ettringite consisted of short, stubby, prismatic crystals, approximately 1 μm in length. No difference was observed between the unheated sample and the partially dehydrated sample.

D. REHYDRATION

Partially dehydrated ettringite was rehydrated in a calorimeter, in order to measure its heat of hydration. Enthalpy changes measured during rehydration, Table III, ranged from 9 calories per gram sample for material dehydrated at 56°C (7% weight loss) to 106 calories per gram sample for material first dehydrated at 110°C (31% weight loss).

In order to compare the change in enthalpy measured during rehydration with the change in enthalpy measured during dehydration, the values must be expressed relative to the amount of water gained or lost. Rehydration values are equivalent to between 130 and 340 calories per gram of water. The changes in enthalpy measured during dehydration by DSC, on the other hand, are equivalent to 460 calories per gram of water. Therefore, the heat of rehydration is somewhat less than the heat of dehydration. This difference is attributed to the partial

prehydration of the sample during hydration calorimetry. More accurate determination of the heat of rehydration will be an objective during the remainder of the program.

E. HYDROTHERMAL DEHYDRATION/REHYDRATION

Hydrothermal reactions of the Fe-substituted ettringite were measured by DSC, in which the sample was immersed in water in a high-pressure cell. These results, summarized in Table IV, were quite different than the results in open pans at atmospheric pressure. After the first hydrothermal heating, cycles produced an exotherm on cooling and endotherm on heating, at a temperature of approximately 50°C, and an enthalpy change of approximately 4 calories per gram sample. The reaction was studied for 3 cycles, during which it was fully reversible.

However, studies by Satava and Veprek (14) suggest that the hydrothermal reaction is not dehydration, but rather conversion of ettringite to a mixture of monosulfate and calcium sulfate hemihydrate. If so, the reaction is not congruent, in that solid ettringite is being converted to two other solids. An incongruent reaction is less suitable for application in energy storage, in that the reaction products may segregate, limiting the efficiency of the material.

IV. CONCLUSIONS

Significant progress has been made on the study of ettringite as an energy storage material. Although the program is still in progress, several important conclusions have been reached:

(1) Procedures for rapid synthesis of ettringite have been developed, which may be modified in order to synthesize ettringite-like phases with various chemical substitutions. Ettringite-like phases were synthesized with the following substitutions: CO_3 for SO_4, Fe for Al, and Cr for Al. The following substitutions were not successful: Si for Al, and Cl or NO_3 for SO_4.

(2) Values for heat capacity for ettringite and substituted ettringite-type phases were approximately 0.3 calories per gram per degree Celcius. There was no significant difference in values of heat capacity for the various phases.

(3) Dehydration of ettringite-type phases at atmospheric pressure occurred over a temperature range from approximately 30°C to approximately 55°C. The upper temperature was different for each substituted phase, lowest (49°C) for the CO_3-substituted ettringite, and highest (58°C) for the Fe-substituted ettringite. Measured enthalpy changes ranged between 100 and 240 calories per gram of sample. Thus the material has good potential as a phase change material for solar energy storage.

(4) Rehydration of dehydrated phases at room temperature produced an enthalpy change of approximately 100 calories per gram sample, somewhat less than the enthalpy change during dehydration of the same material. It is not clear

whether the discrepancy results from experimental difficulties or indicates that the rection is not fully reversible.

(5) Hydrothermal reaction of ettringite occurred at approximately 50°C with an enthalpy change of approximately 4 calories per gram sample. The reaction appears to be fully reversible in 3 cycles.

V. FUTURE WORK

During the remainder of the program, the following work will be completed. Replicate measurements of the enthalpy change due to dehydration will be made, in order to determine if the differences in enthalpy changes measured for the different ettringite-like phases are significant. Rehydration experiments will be continued, in order to determine how reversible is the dehydration at atmospheric pressure. Finally, experiments on the hydrothermal reaction will be continued.

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TABLE I

HEAT CAPACITY

Phase	c_p calories/gram/°C
$[Ca_3Al(OH)_6]_2(SO_4)_3 \cdot 26H_2O$	0.31
$[Ca_3Fe(OH)_6]_2(SO_4)_3 \cdot 26H_2O$	0.29
$[Ca_3Cr(OH)_6]_2(SO_4)_3 \cdot 26H_2O$	0.32
$[Ca_3Al(OH)_6]_2(CO_3)_3 \cdot 26H_2O$	0.30

TABLE II

DEHYDRATION RESULTS

Phase	Temperature (°C)	Loss (moles H_2O)	ΔH (calories/gram)
$[Ca_3Al(OH)_6]_2(SO_4)_3 \cdot 26H_2O$	40-51	20	120
$[Ca_3Fe(OH)_6]_2(SO_4)_3 \cdot 26H_2O$	30-58	24	230
$[Ca_3Cr(OH)_6]_2(SO_4)_3 \cdot 26H_2O$	30-55	13	120
$[Ca_3Al(OH)_6]_2(CO_3)_3 \cdot 26H_2O$	32-49	23	100

* Lower temperature is the onset of the dehydration, determined by DSC, and upper temperature is the end of dehydration, determined by TGA.

TABLE III

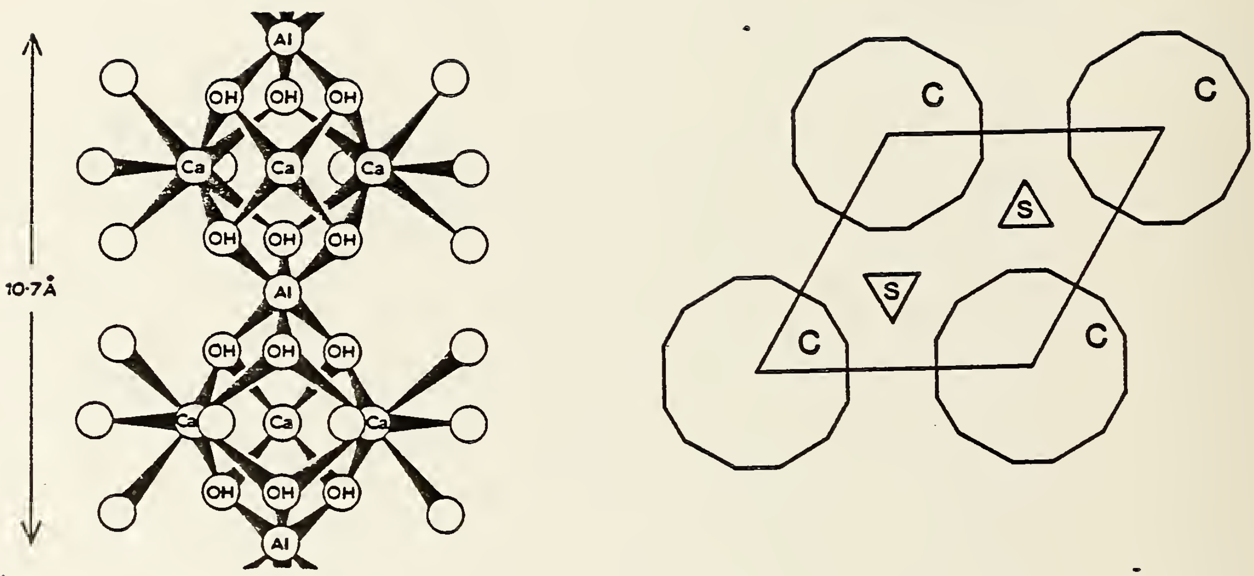
REHYDRATION RESULTS

Dehydration Temperature (°C)	Dehydration Loss (%)	ΔH on Rehydration (calories/gram)
56	7	9
110	24	60
110	31	106

TABLE IV

HYDROTHERMAL REACTION OF Fe-SUBSTITUTED ETTRINGITE

Cycle	Peak Onset (°C)	ΔH (calories/gram)
1 - heating	72 103	+0.5 -0.9
cooling	38	-4
2 - heating	61	+3
cooling	41	-4
3 - heating	60	+3
cooling	41	-5



(a)

(b)

Figure 1. Crystal structure of ettringite, from Taylor (3); a) column of hydrated calcium aluminate, projected on $(11\bar{2}0)$, not showing the water molecules that are bound to the column; and b) ettringite channel viewed along the c-axis, with the triangles representing the SO_4 ions and water molecules within the channel.

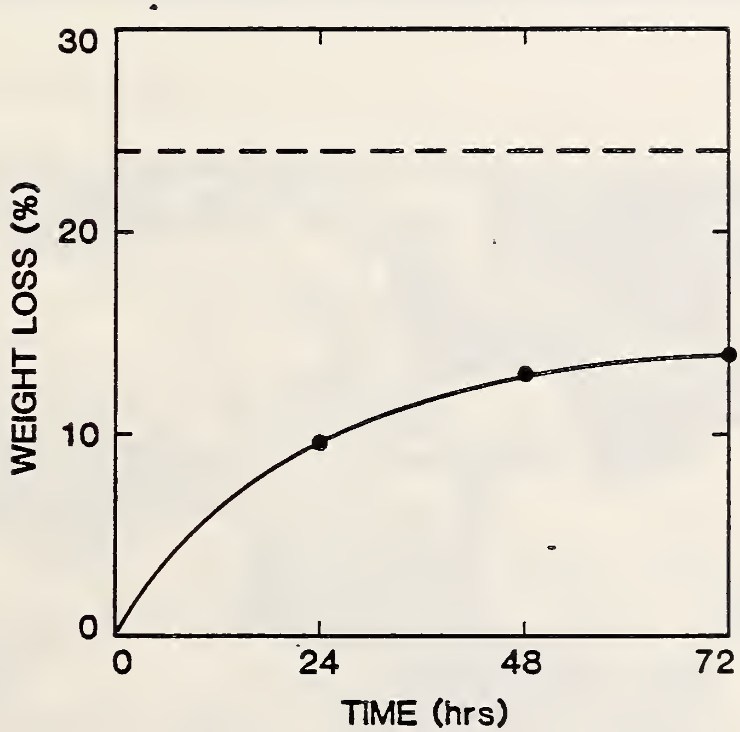
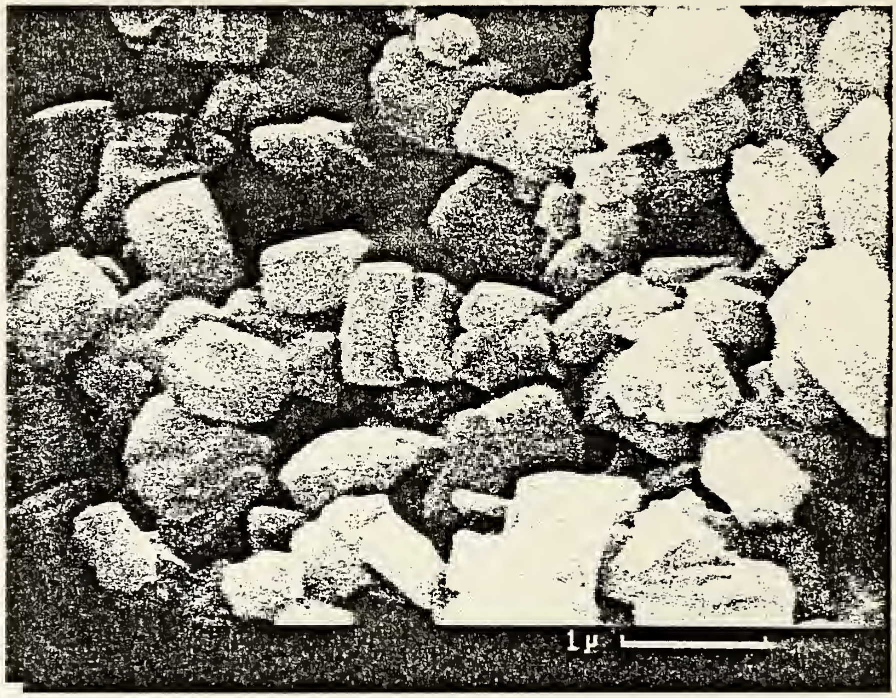
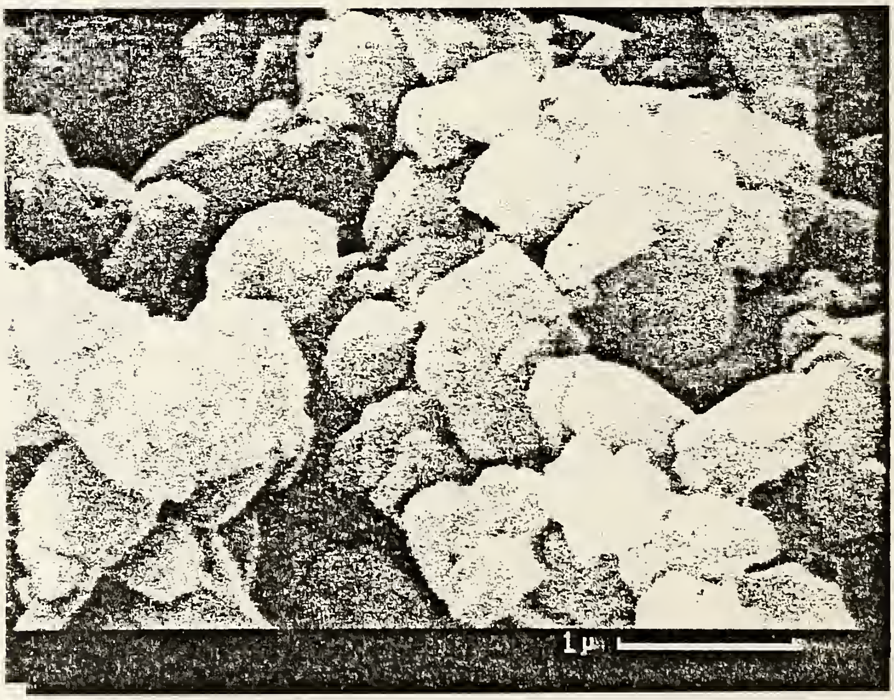


Figure 2. Rate of dehydration of a large sample (several grams) of ettringite at 56°C; dashed line prepresents the weight loss of the 1 mg TGA sample.



(a)



(b)

Figure 3. Scanning electron micrographs of (a) ettringite, and (b) ettringite heated 48 hours at 56°C (13% weight loss).

APPENDIX A

SYNTHESIS PROCEDURES

A-1. Ettringite.

Solution I: 13.63 grams $Al_2(SO_4)_3$, dissolved in 40 ml H_2O.

Solution II: 13.40 grams CaO, dissolved in 890 ml aqueous 10% sugar solution.

Mix solutions I and II. Rotate for several hours or overnight. Filter.

A-2. Fe-substituted ettringite.

Slurry I: 15.92 grams $Fe_2(SO_4)_3$, suspended in 1000 ml H_2O.

Solution II: 12.82 grams CaO, dissolved in 850 ml aqueous 10% sugar solution.

Mix slurry I and solution II. Rotate for one day or longer. Filter.

A-3. Cr-substituted ettringite.

Solution I: 38.26 grams $CrK(SO_4)_2 \cdot 12H_2O$, dissolved in 20 ml H_2O.

Solution II: 12.89 grams CaO, dissolved in 1000 ml aqueous 10% sugar solution.

Mix solutions I and II. Rotate for several hours or overnight. Filter.

A-4. CO_3-substituted ettringite.

Solution I: 9.66 grams $Na_2Al_2O_4 \cdot 3H_2O$, dissolved in 140 ml H_2O. Add and dissolve 11.15 grams $NaHCO_3$.

Solution II: 14.91 grams CaO, dissolved in 990 ml aqueous 10% sugar solution.

Mix solutions I and II. Rotate a few hours or overnight. Filter.

A-5. Si- and CO_3-substituted ettringite (thaumasite, unsuccessful).

Solution I: 9.80 grams Na_2SiO_3, dissolved in 150 ml H_2O. Add and dissolve, 25.88 grams $Na_2SO_4 \cdot 10H_2O$ and 8.51 grams Na_2CO_3.

Solution II: 13.51 grams CaO, dissolved in 930 ml aqueous 10% sugar solution.

Cool solutions to 5°C. Mix solutions I and II. Store for a few hours at 5°C. Filter. Product was amorphous.

A-6. Cl-substituted ettringite.

Solution I: 20.46 grams $AlCl_3 \cdot 6H_2O$, dissolved in 100 ml H_2O.

Solution II: 14.26 grams CaO, dissolved in 950 ml aqueous 10% sugar solution.

Mix solutions I and II. Rotate for a few hours. Filter. Product was AFm rather than ettringite.

A-7. NO_3-substituted ettringite.

Solution I: 28.01 grams $Al(NO_3)_3 \cdot 9H_2O$, dissolved in 100 ml H_2O.

Solution II: 12.56 grams CaO, dissolved in 860 ml aqueous 10% sugar solution.

Mix solutions I and II. Rotate for a few hours. Filter. Product was amorphous.

APPENDIX B

X-RAY DIFFRACTION PATTERNS

This appendix contains X-ray diffraction patterns for ettringite and the various substituted ettringite-type phases.

All XRD patterns were collected by powder diffractometer using CuK_{α} radiation.

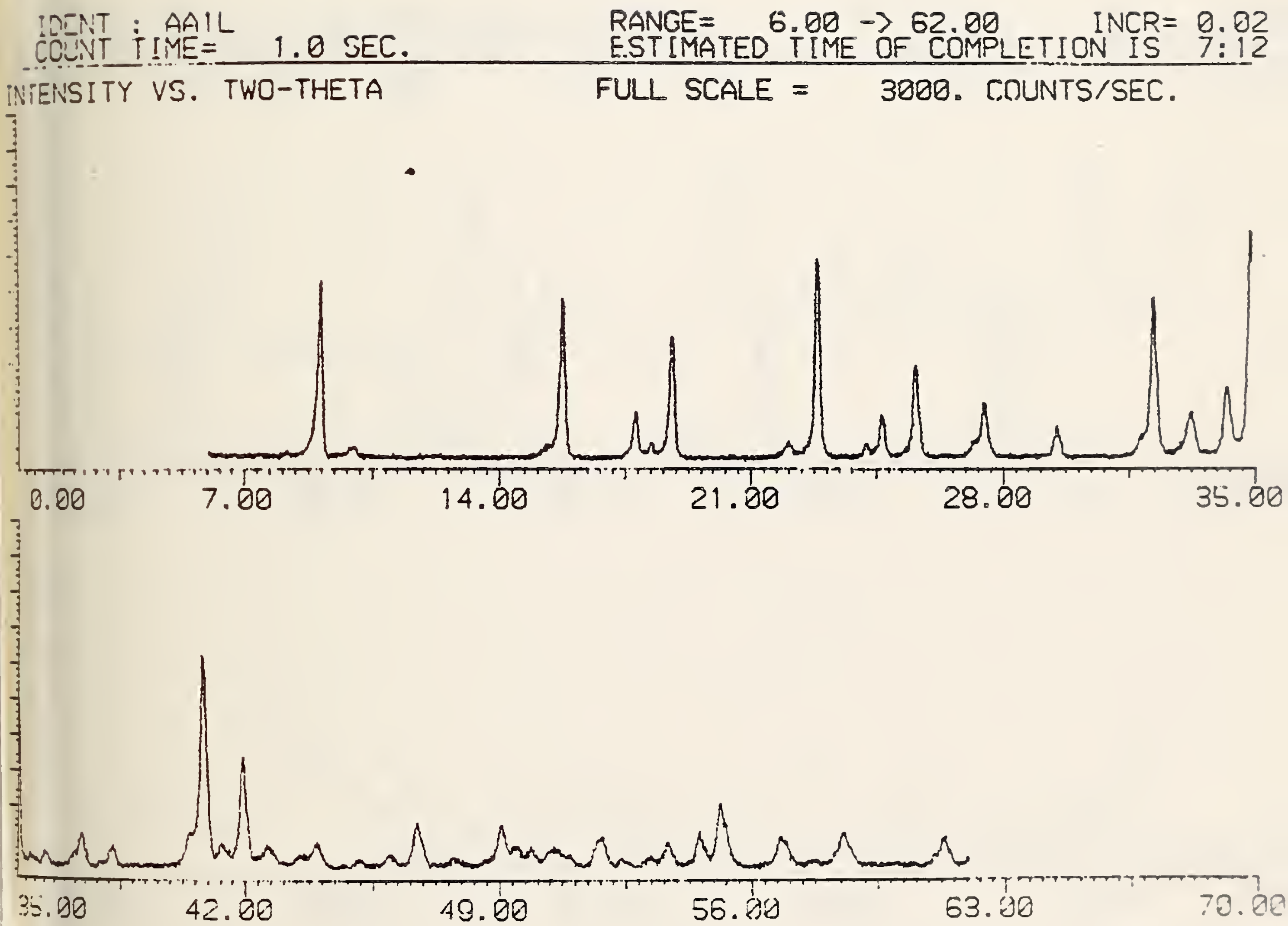


Figure B-1. Ettringite.

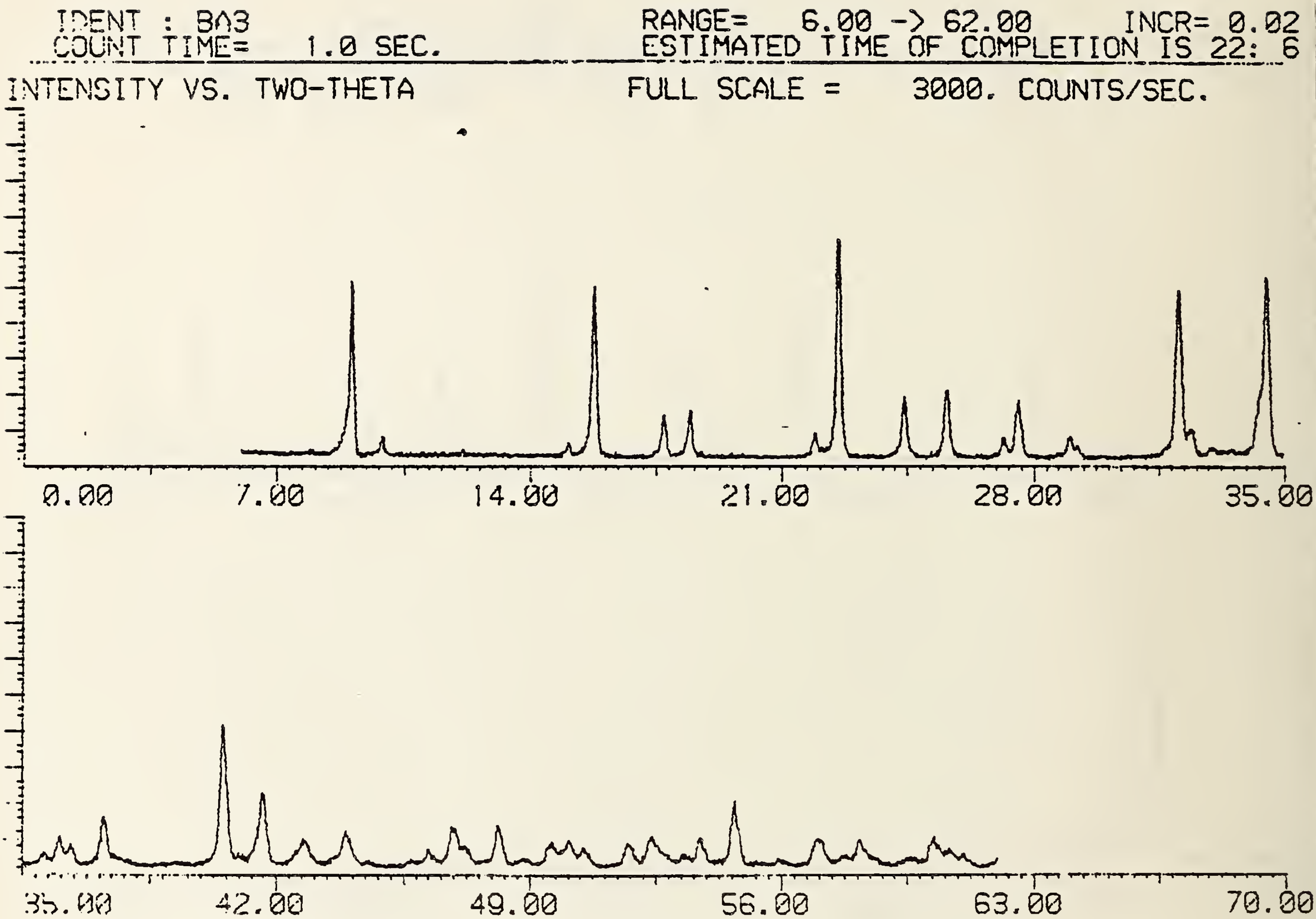


Figure B-2. Fe-substituted ettringite.

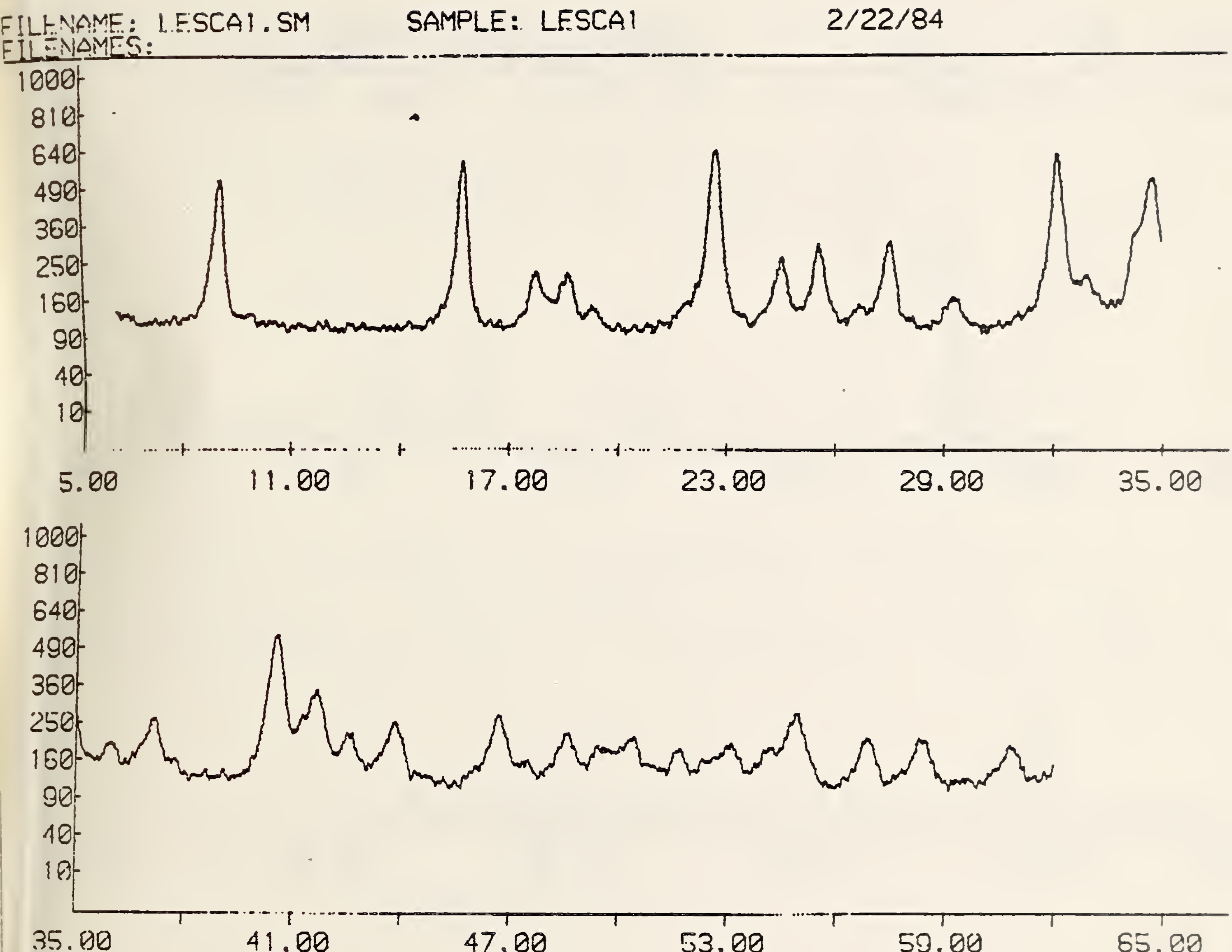


Figure B-3. Cr-substituted ettringite.

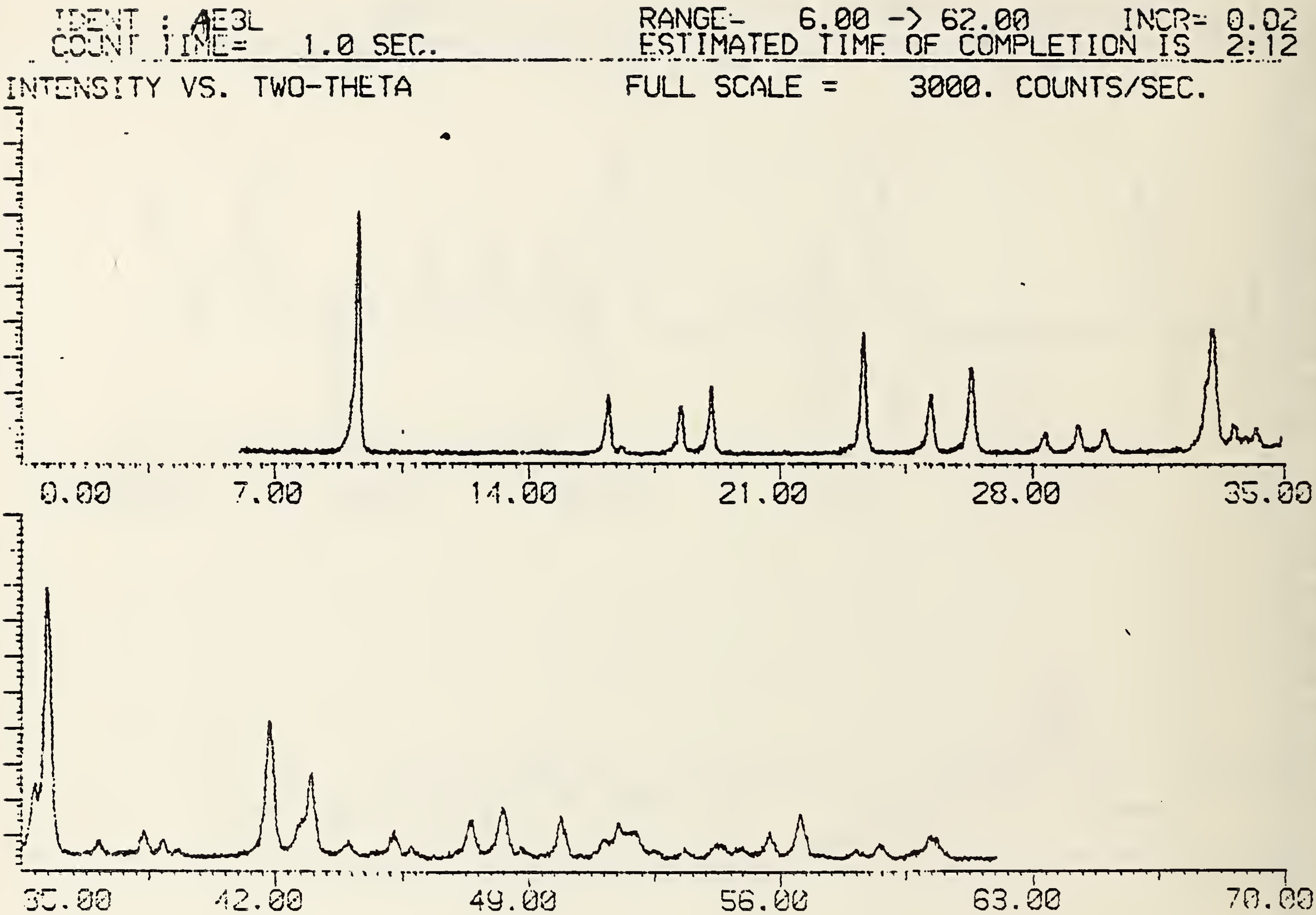


Figure B-4. CO_3-substituted ettringite.

APPENDIX C

TGA CURVES

This appendix contains TGA curves for dehydration in an open pan of ettringite and substituted ettringite-type phases.

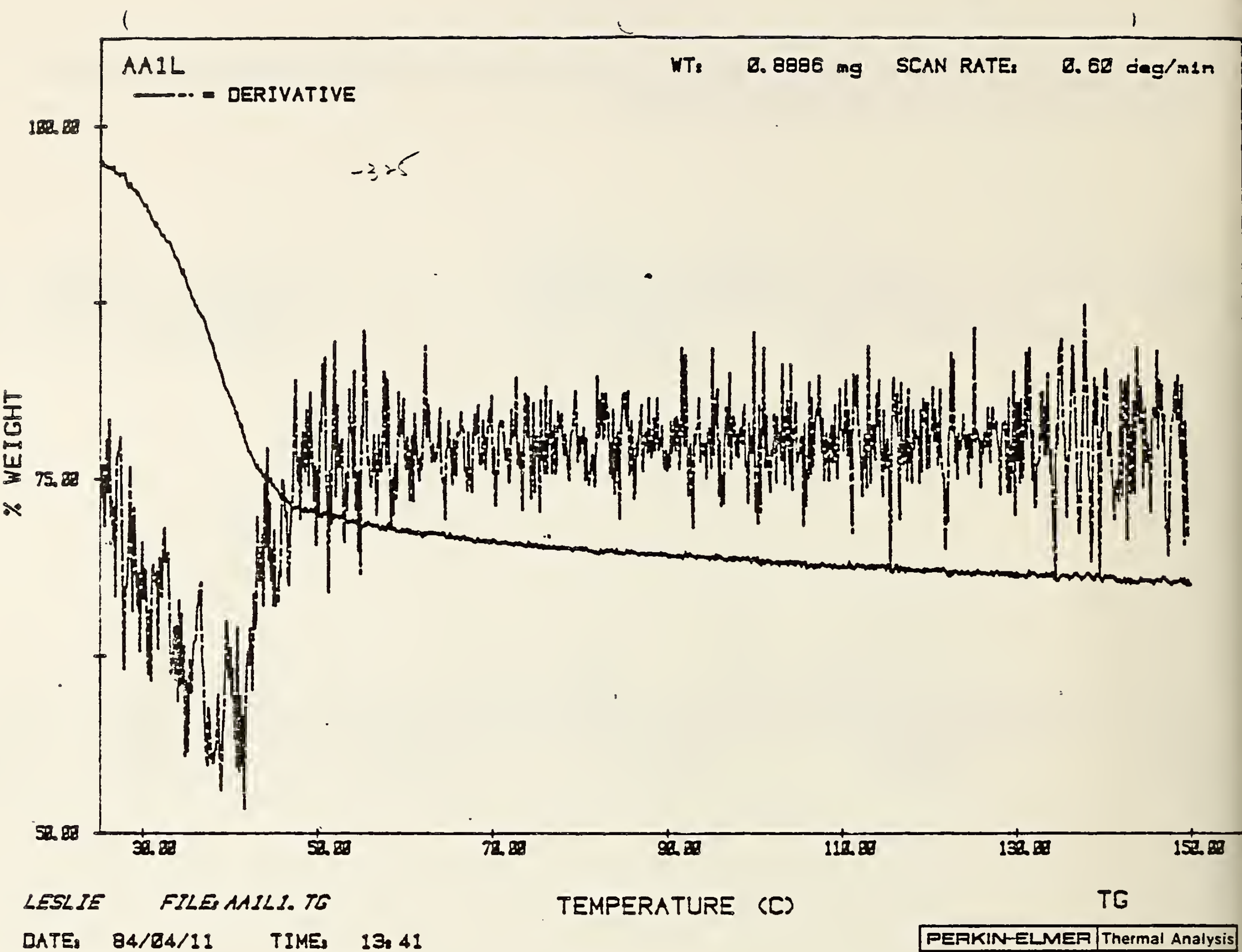


Figure C-1. Ettringite.

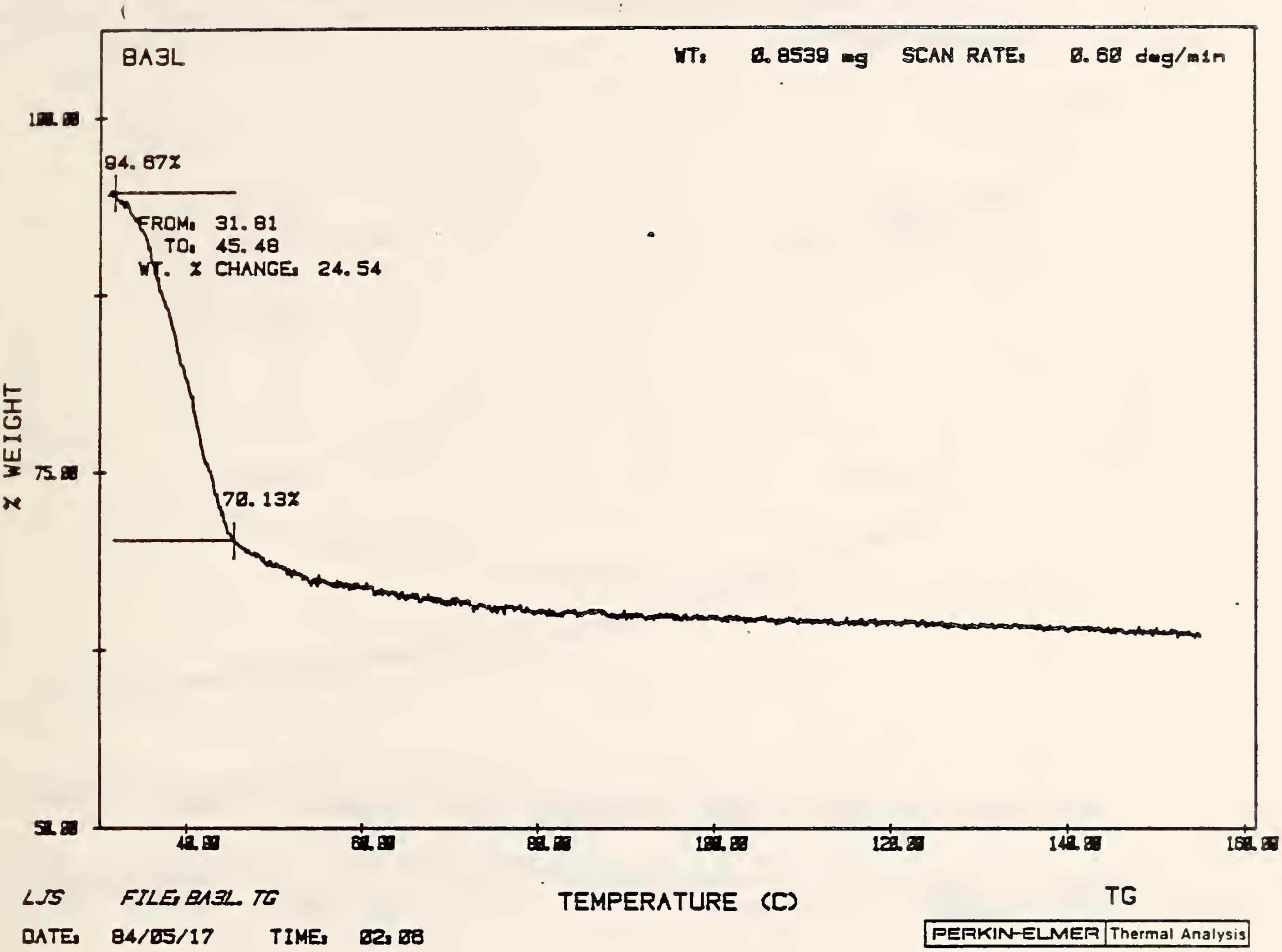


Figure C-2. Fe-substituted ettringite.

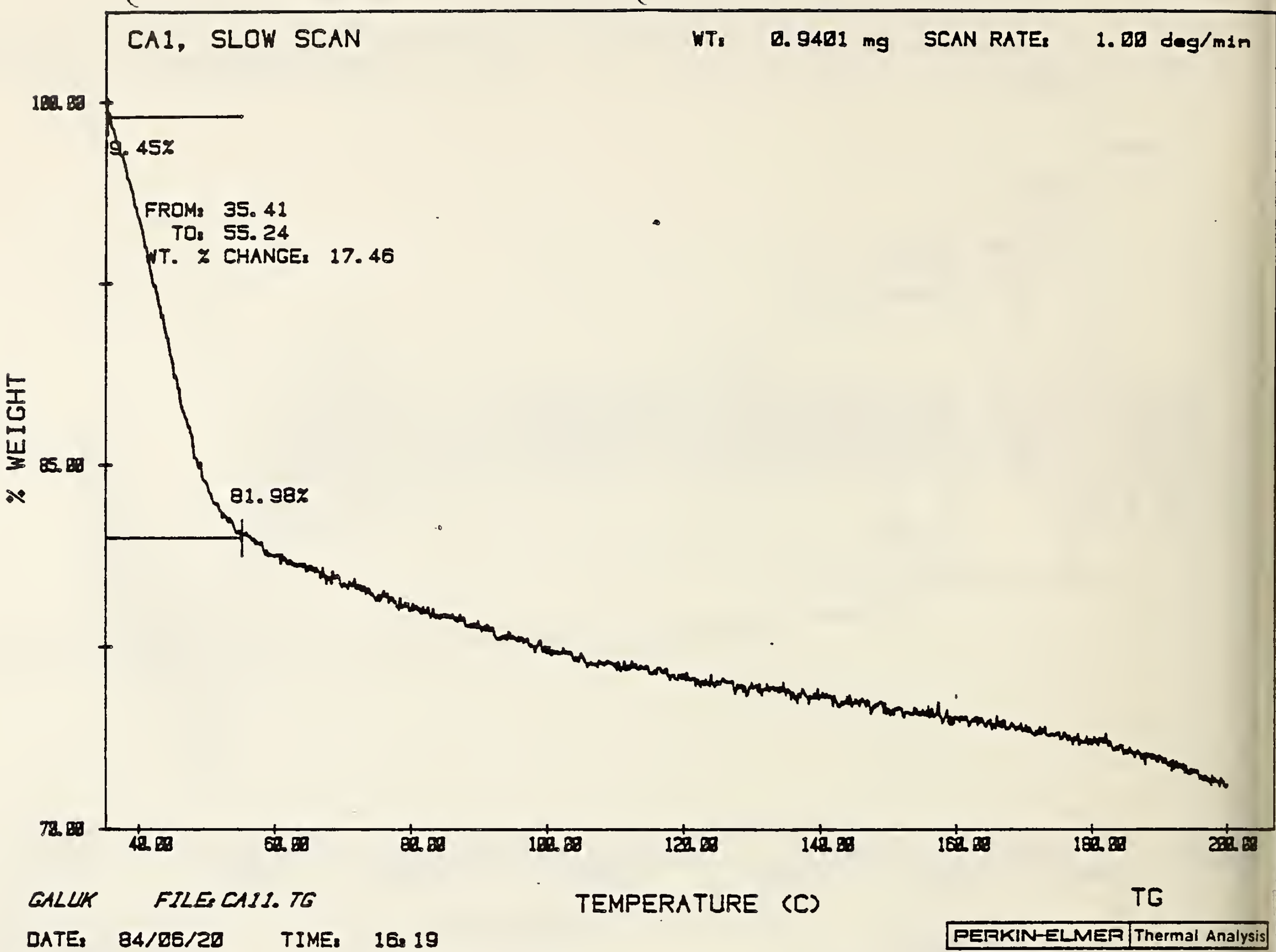


Figure C-3. Cr-substituted ettringite.

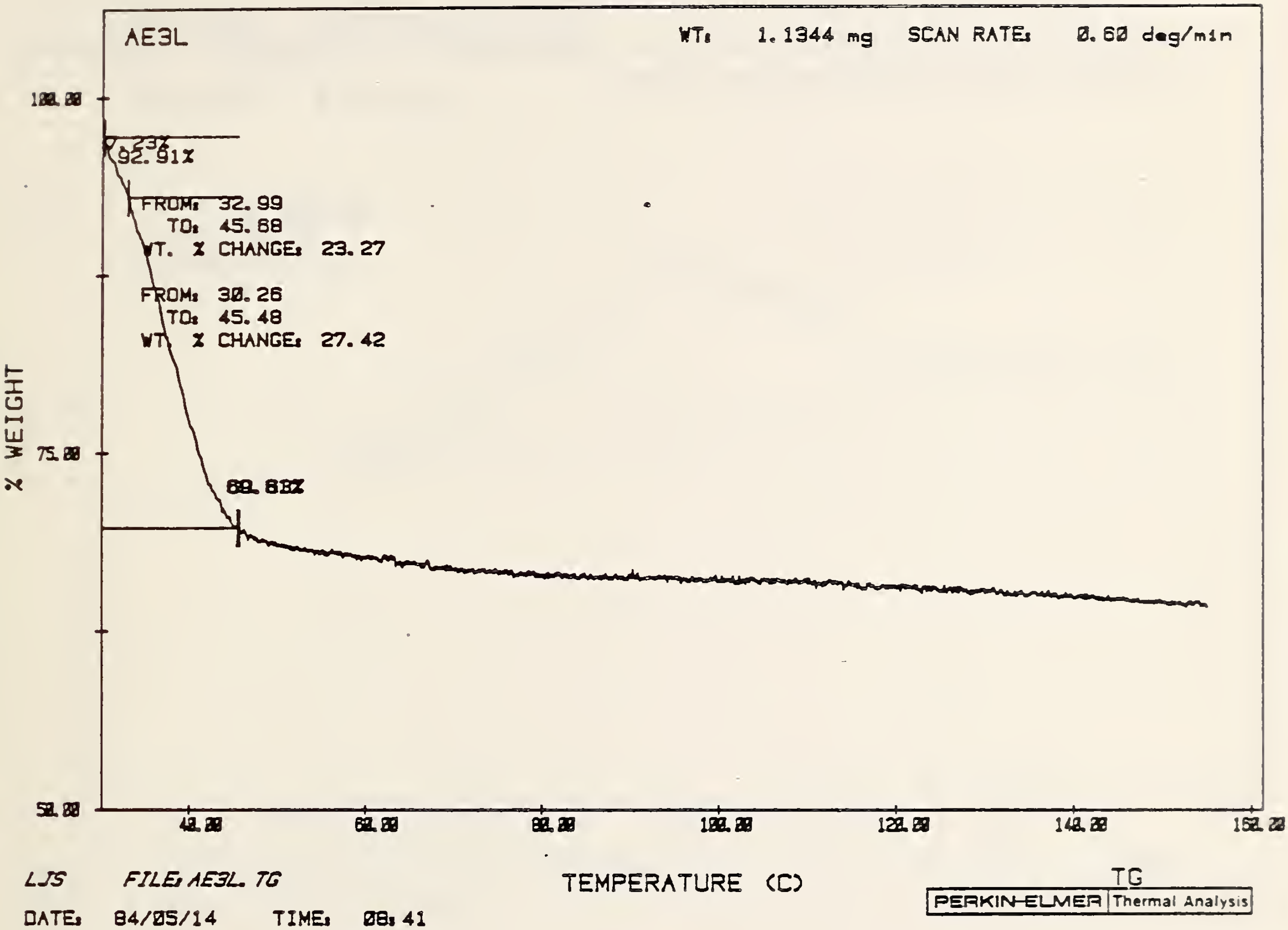


Figure C-4. CO_3-substituted ettringite.

APPENDIX D

DSC CURVES

This appendix contains DSC curves for dehydration in an open pan of ettringite and substituted ettringite-type phases.

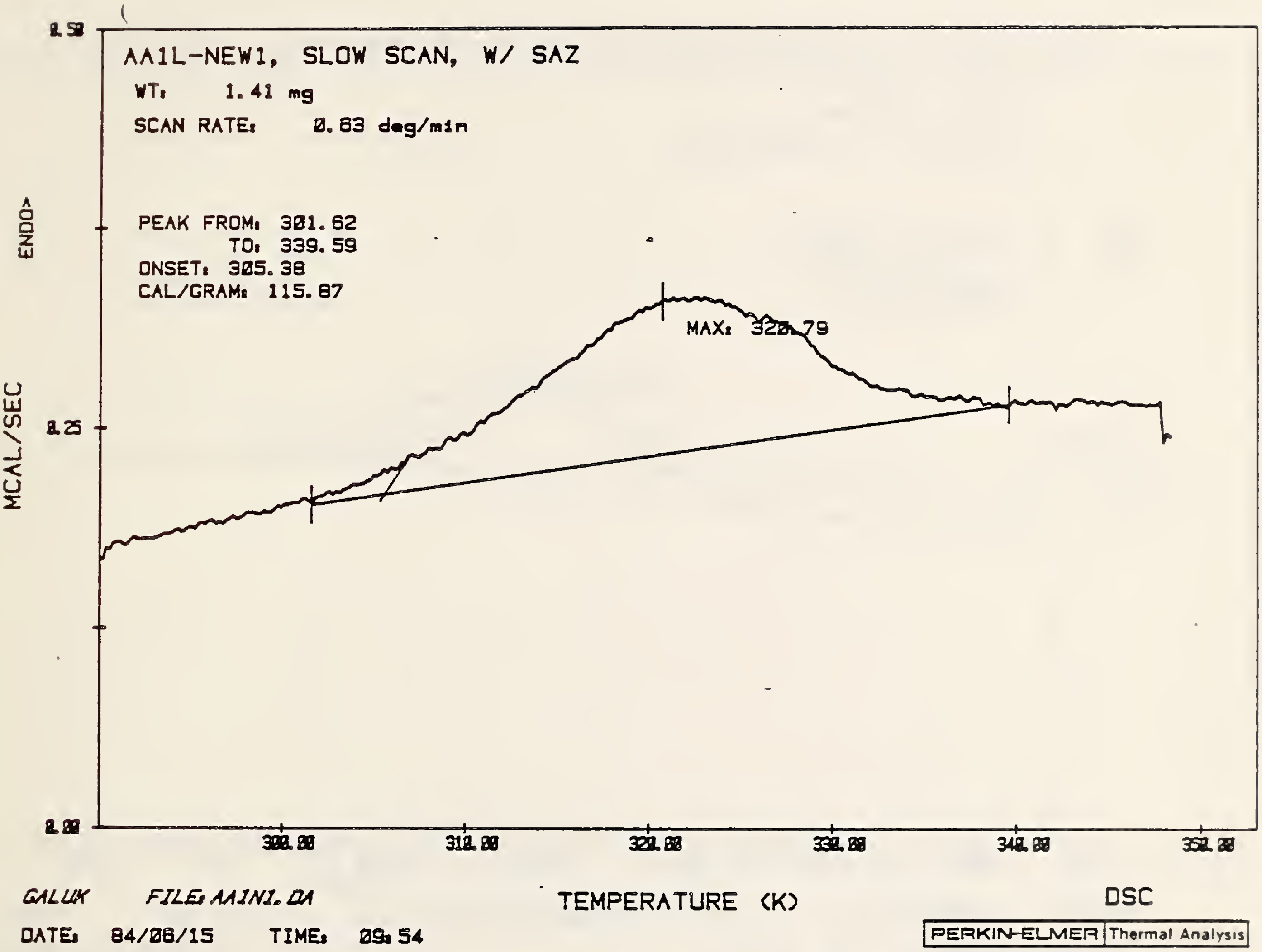


Figure D-1. Ettringite.

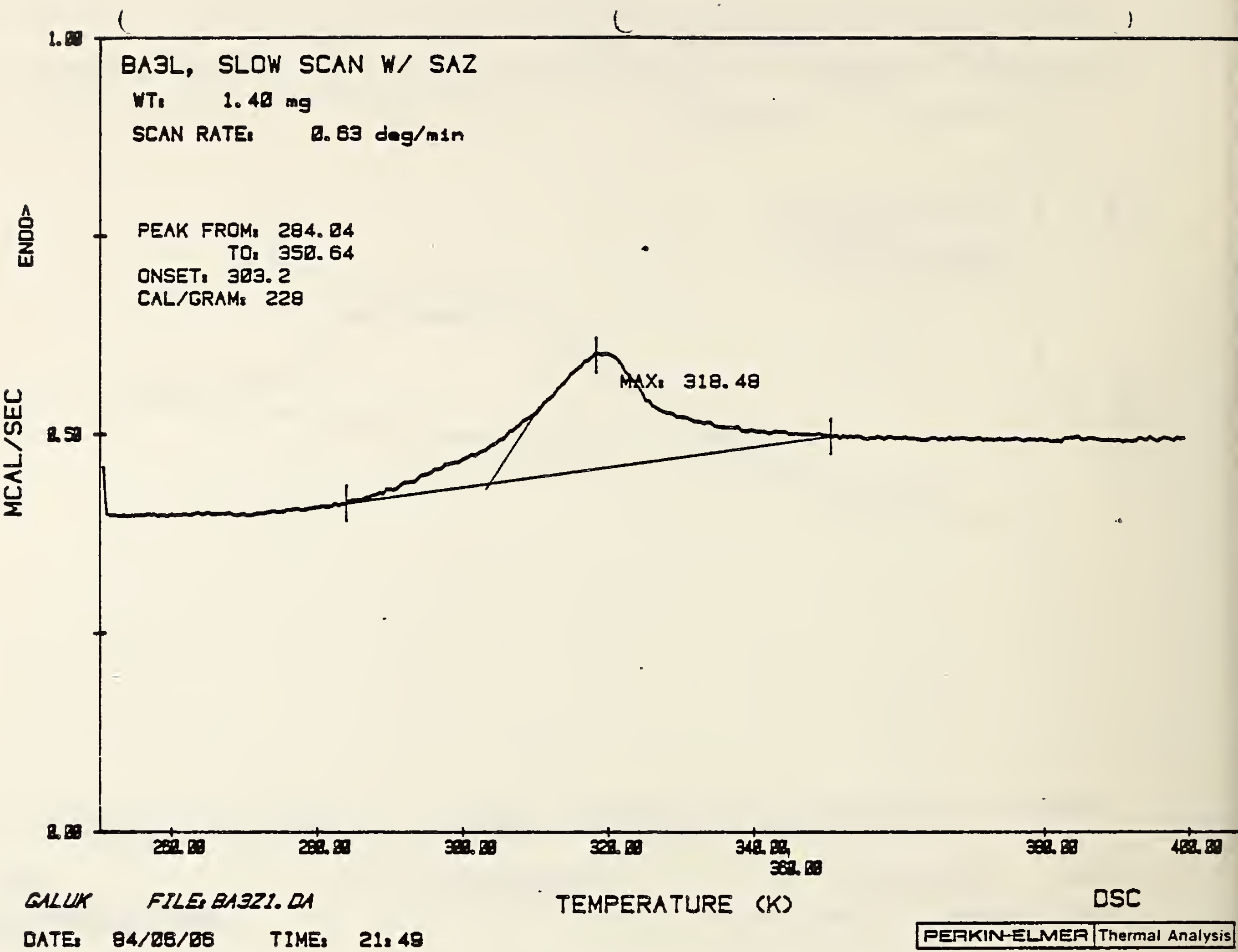


Figure D-2. Fe-substituted ettringite.

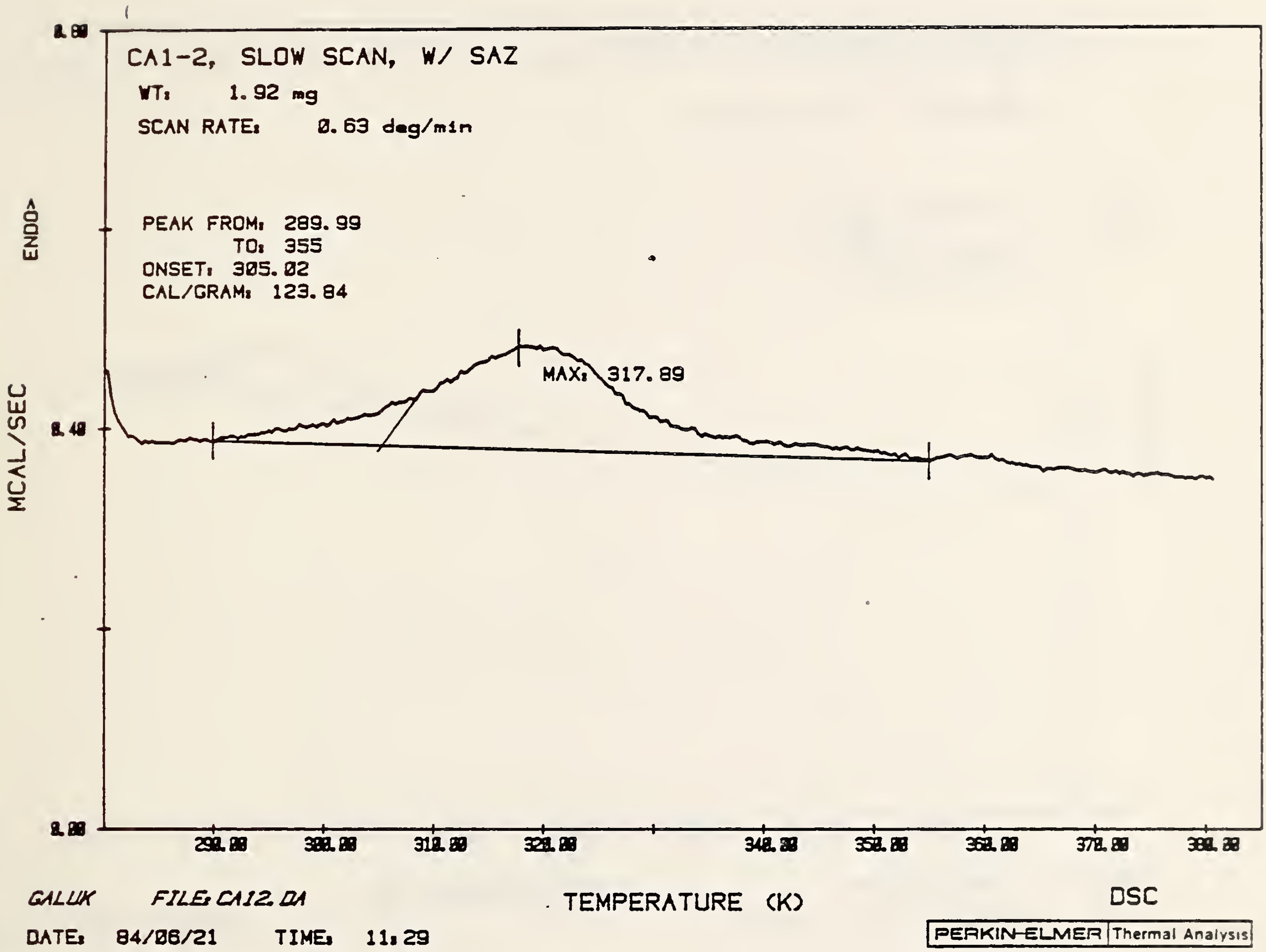


Figure D-3. Cr-substituted ettringite.

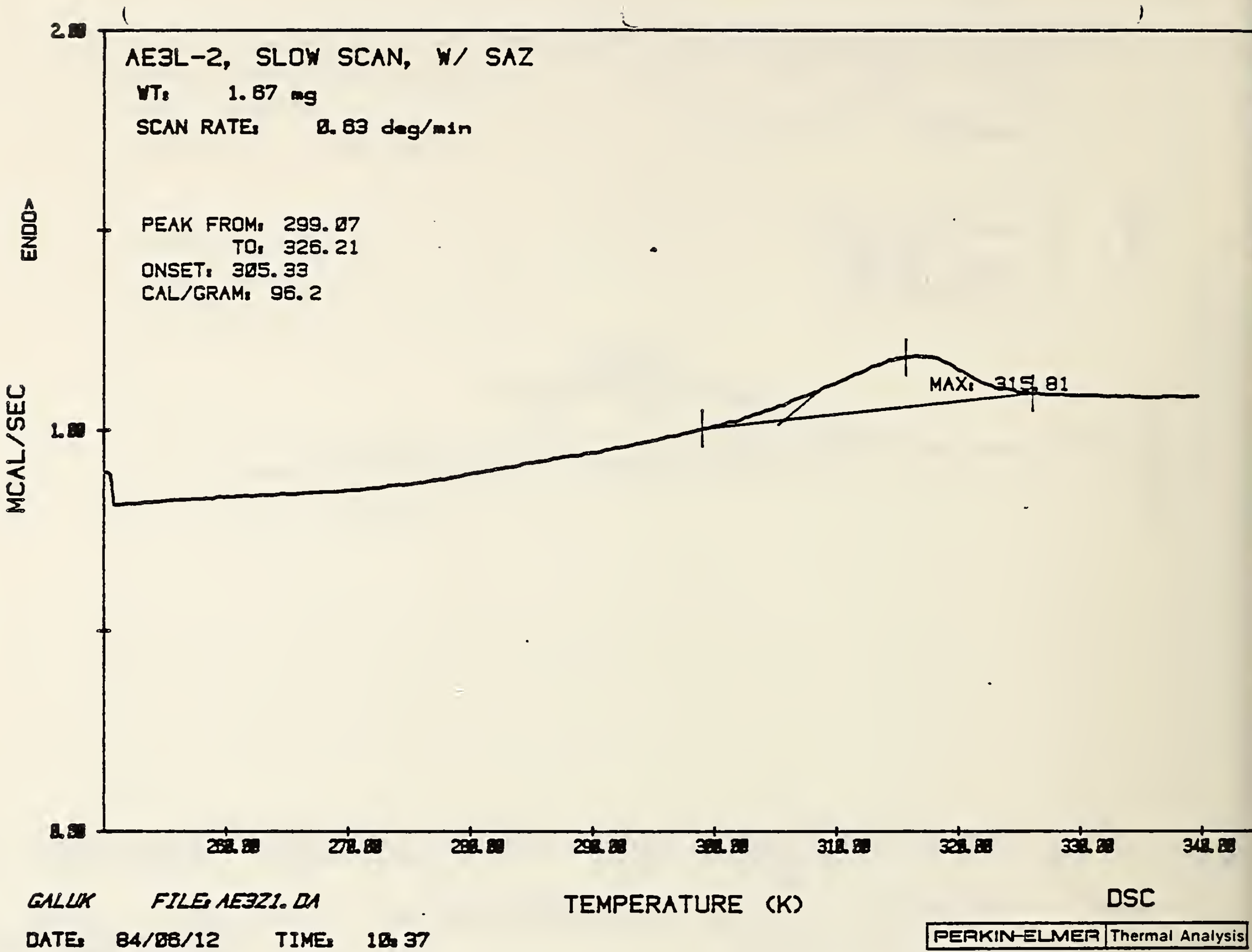
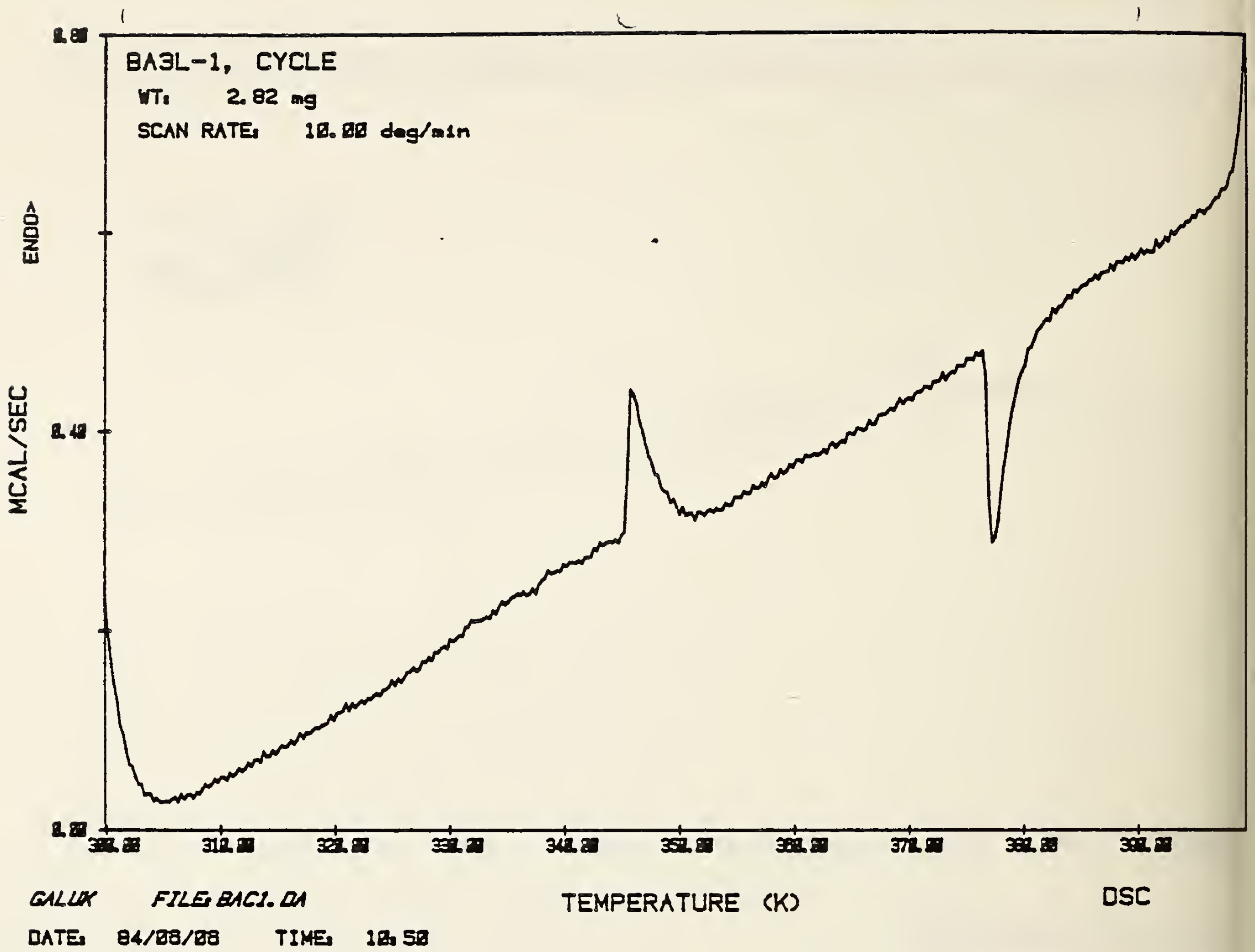


Figure D-4. CO_3-substituted ettringite.

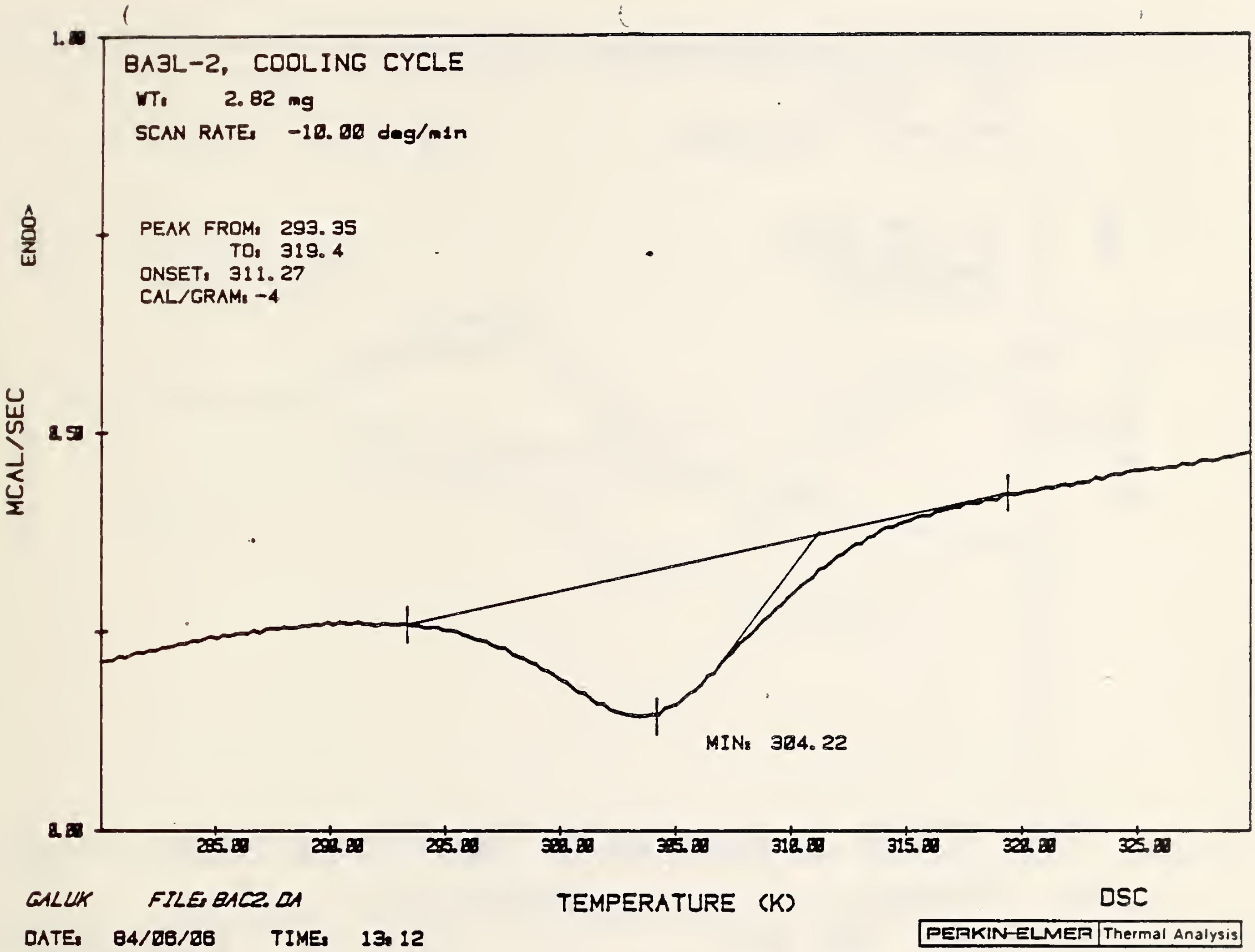
APPENDIX E

HYDROTHERMAL DSC CURVES

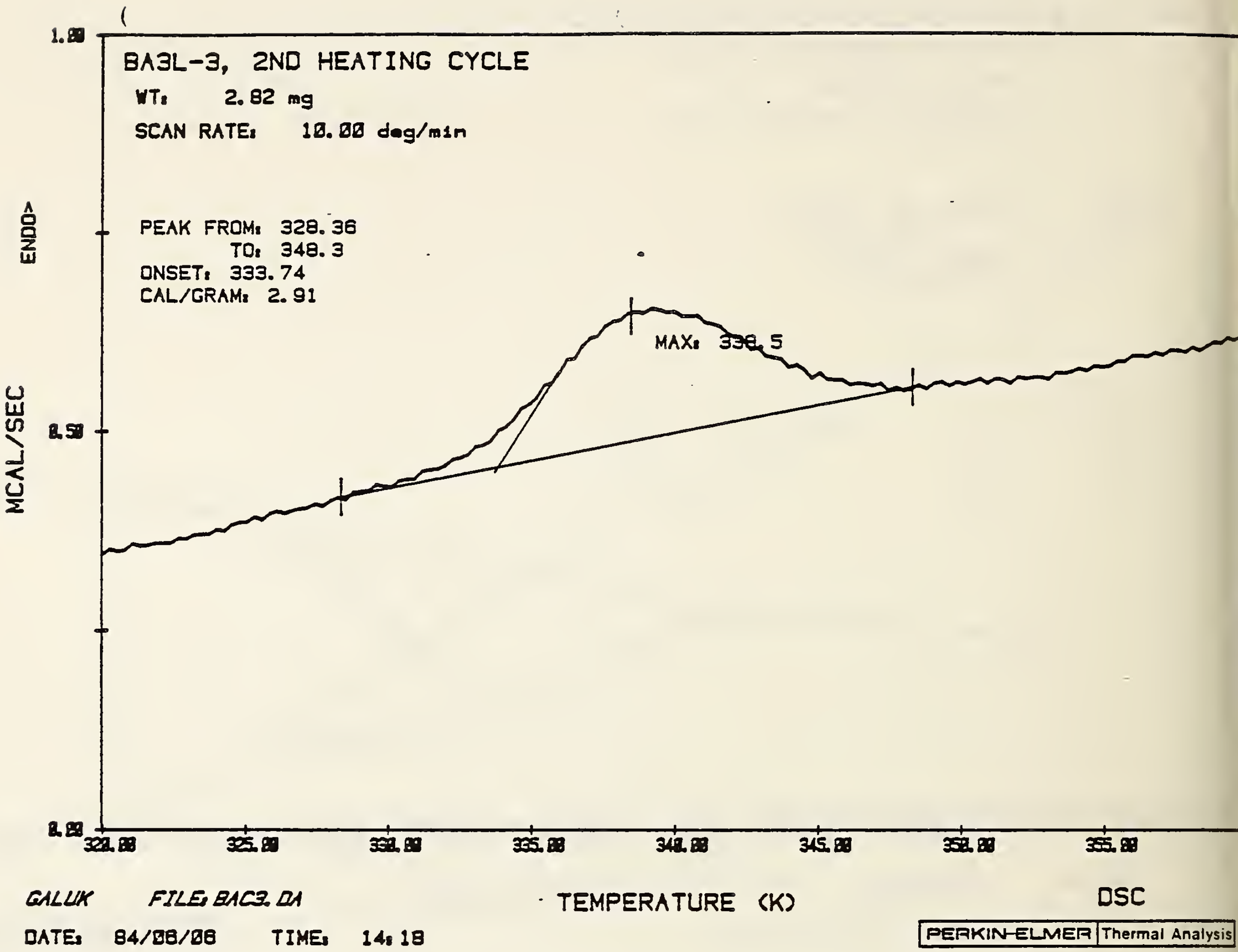
This appendix contains the curves for hydrothermal reaction of Fe-substituted ettringite.



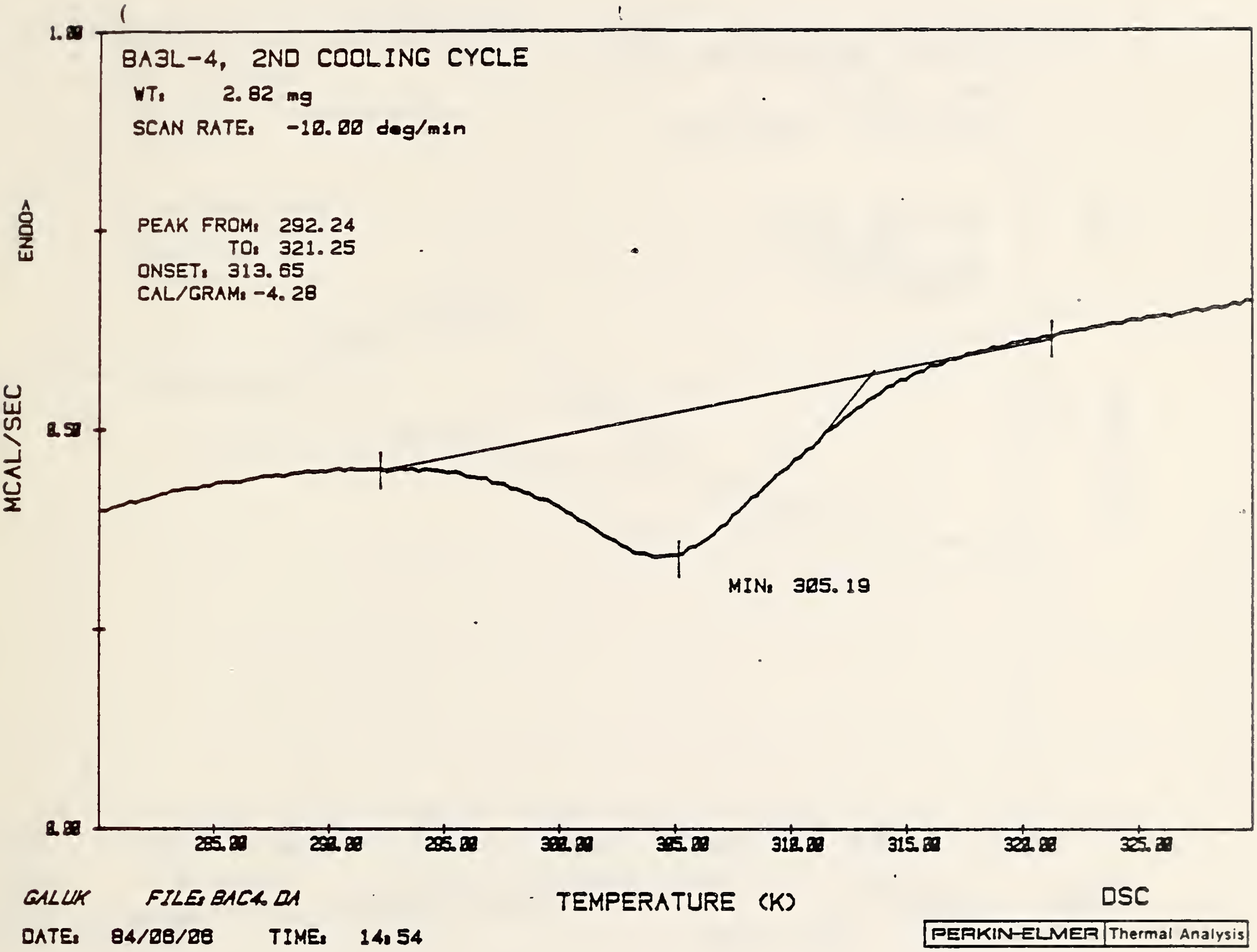
E-1. First cycle, heating.



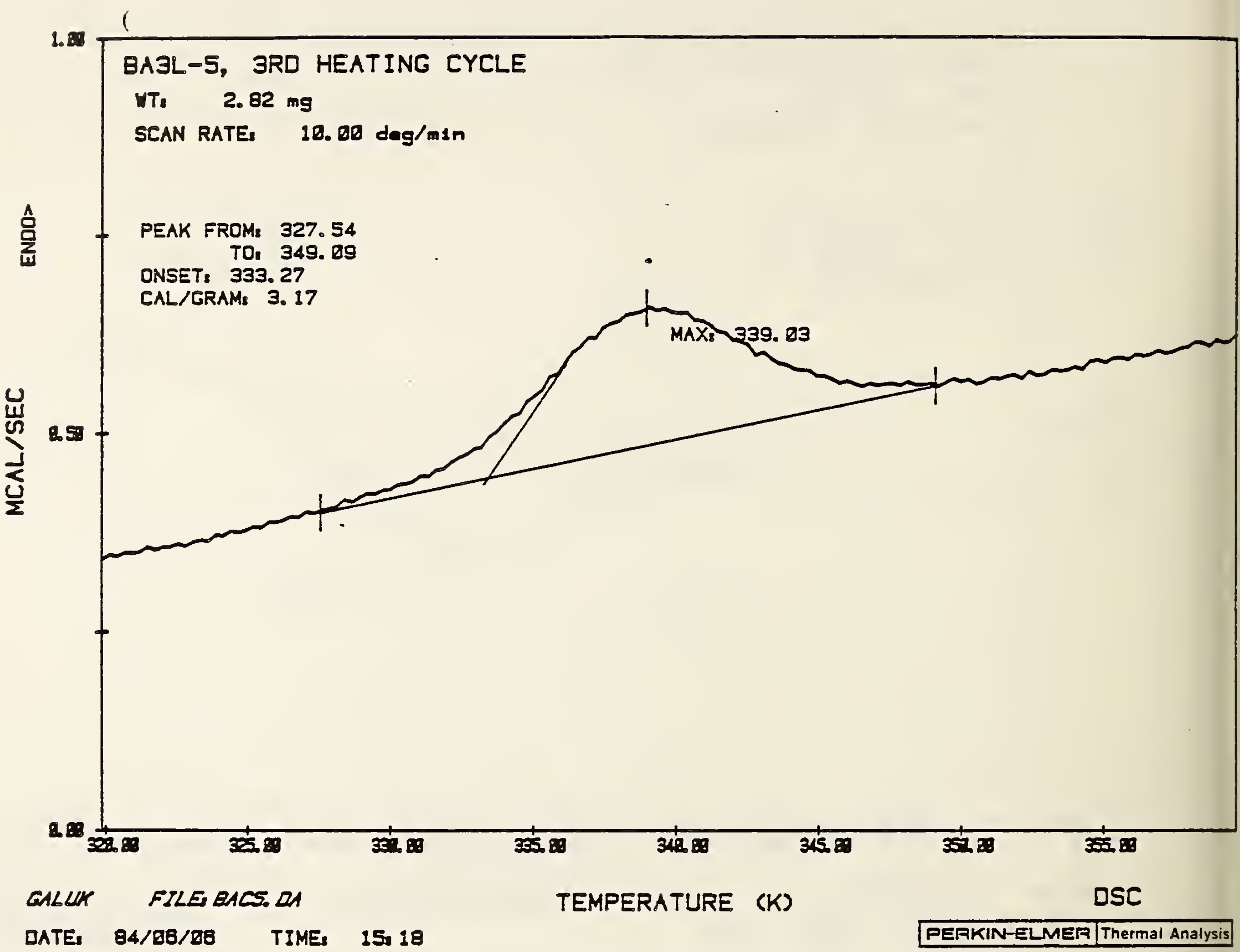
E-2. First cycle, cooling.



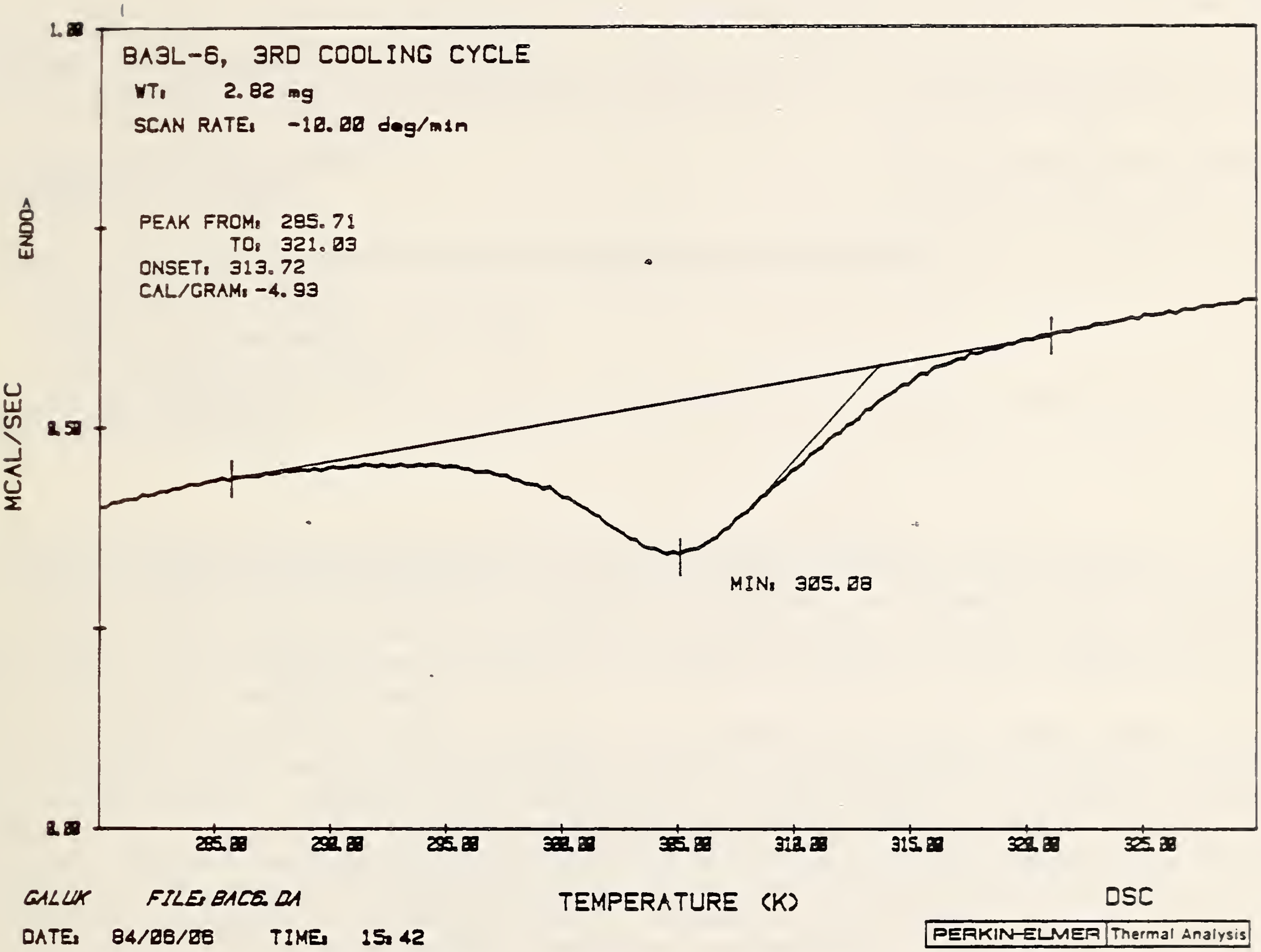
E-3. Second cycle, heating.



E-4. Second cycle, cooling.



E-5. Third cycle, heating.



E-6. Third cycle, cooling.

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Leslie J. Struble and Paul W. Brown

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10. SUPPLEMENTARY NOTES

☐ Document describes a computer program; SF-185, FIPS Software Summary, is attached.

11. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)

This report describes an investigation of ettringite and related phases for potential application in solar energy storage. The specific objective is to evaluate the potential of ettringite dehydration and rehydration as a phase change for energy storage.

Synthesis procedures have been developed, and a number of ettringite-type phases have been prepared. The heat capacity of each phase was approximately 0.3 calories per gram per degree Celcius. Studies of the dehydration of these phases at atmospheric pressure indicate that the material has good potential as a phase change material for solar energy storage. Dehydration occurred at temperatures in the range between approximately 30°C and 55°C, with changes in enthalpy ranging between 100 and 240 calories per gram sample. In addition, ettringite was found to have a reversible hydrothermal reaction at approximately 50°C, with an enthalpy change of approximately 4 calories per gram sample.

Future work during the remainder of this program will involve completing the work described in the present progress report.

12. KEY WORDS (Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)

AFt; enthalpy change; ettringite; phase change material; solar energy storage

13. AVAILABILITY

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